LOSS OF ALKALI OXIDE FROM BETA" ALUMINA
AND ITS IMPORTANCE TO AMTEC LIFE ISSUES

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ABSTRACT

Loss of sodium oxide into a gas phase comprised of low to high pressure sodium at typical AMTEC operating conditions does notseemi ndicatedasa life limiting step under projected conditions. Sodium oxide loss is strongly thermally activated and strongly suppressed by external sodium gas pressure. However, loss of sodium oxide into liquid sodium may be, but is not clearly known to be, much more rapid than loss into the gas phase and could result both BASE degradation and enhanced corrosion of other AMTEC components. This favors conservative selection of vapor-fed cell designs and may significantly influence materials selection and use of getters.

INTRODUCTION

AMTEC cells have been considered an attractive power source for a variety of long term robotic NASA missions. Several AMTEC cells have now been operated for period over one year. A large number of cells have been operated for shorter but still substantial periods of time >1000 hours. Substantial development of vapor-fed cells has occurred. Series connected AMTEC multi-cells have been built and operated at Ford, AMPS, JPL, and the Electrotechnical Laboratory. Work at J] '[, has addressed lifetime testing rrnd modeling for the external electrode, which is a critical component which must function with minimal losses for good AMTEC performance. Tests of sodium and potassium beta" alumina conductivity on exposure to alkali metal vapor at 1125 -1200K for 1500 and 500 hours respectively have been reported, with no observation of sustained degradation

Loss of refractory materials by evaporation and chemical transformations in the high temperature zones is a problem common to all heat engines. In the case of AMTEC cells, a particular volatilization and associated corrosion problem can be identi fied, since background information is available. Alkali oxide loss from beta" alumina at temperatures from out 1500 to 2000K has been reported and slow loss at AMTEC operating conditions is a concern, which is closely related to concerns about aggravated high temperature corrosion of metallic components of AMTECs by alkali oxide in liquid alkali metal at operating temperatures from 900-1300K. If alkali oxide loss continues indefinitely, the beta" alumina solid electrolyte (BASE) ceramic would eventually be destroyed. If alkali oxide equilibrates with a small concentration dissolved in liquid alkali metal, then metallic components which can tolerate alkali oxide in liquid alkali metal must be used. If alkali oxide loss dots not occur or is extremely slow, or occurs only transiently without BASE degradation, getters may be employed to remove oxide from the liquid metal and the corrosion issue wil I be less severe and allow more flexible selection of component materials. Alkali oxide loss may be expected to be fastest to oxiJc-free liquid alkali metal, slower to vacuum or low pressure alkali metal vapor, and very inhibited to high pressure alkali metal vapor. If loss to liquid metal is fast, vapor fed cel Is become much more favorable candidates for long term applications. At present, calculations of alkali oxide loss can be performed assuming a rate limited only by the thermodynamics of the chemical transformations involved; these results are based on thermodynamic data which is not precise, and this approach does not consider rate limitations imposed by chemical kinetics,

Two of the most important mechanisms of interest in the prediction of long term performance of AMTEC cells are closely related "l hese mechanisms are 1) the loss of alkali oxide from the beta" alumina solid electrolyte (BASE) and 2) the acceleration of corrosive attack on metal and ceramic components by alkali oxide dissolved in alkali metal, If loss of oxygen from the solid electrolyte is sufficiently slow, getters

such as Zr and I If may be employ! to scavenge trace oxygen and allow much greater flexibility in fabrication materials, since most metals are significantly more rapidly attacked in liquid sodium containing significant sodium oxide, compared with very pure liquid sodium. (Foust, 1972; DiStefano, 1989) This paper will present a calculation of the expected rate of oxygen loss from sodium beta/beta" alumina solid electrolyte, Na-BASE, and briefly discuss review the associated chemistry, the role of Na2O on corrosion of metallic and ceramic materials which might be used in AMTEC cell fabrication, and approaches to accelerated testing.

CALCULATIONS AND DISCUSSION

Volatization of Na₂O

Studies of the activity of NaO in beta alumina or beta" alumina mixtures with alpha alumina have been the principal means to derive the free energy of formation of the beta or beta" alumina phases. (Nafe, 1996; Rog et al 1992) These studies assumed that the systems were based on the two components: Na₂O and Al₂O₃; furthermore, the studies generally ignored the presence of spinel block stabilizing oxides and variations in beta and beta" composition While the first assumption is valid with respect to the solid phases in which the oxidation states of Al and Na are constant, the low pressure vapor phase is a disproportionated mixture of Na$_{(g)}$ and O$_{2(g)}$. The influence of stabilizing ions and composition is important but requires much more detailed investigations for complete evaluation We use the best available thermochemical information for the stability of the beta and beta"-aluminas to determine the rate of O2 loss, and compare the loss of O₂ and Na from solid Na₂O.(Weber, 1997) Na₂O is not stable as a gas at higher temperatures; its enthalpy of formation is only -35.6 kJ/mole at 298K, and the entropic contribution to free energy greatly favors Na$_{(g)}$ and O$_{2(g)}$ at typical AMTEC operating temperatures. (Wagman et al, 1982)

For the oxygen activity, a$_{(O2)}$, over Na₂O or over a solid phase in equilibrium with Na₂O:

$$Na_2O(c) \longrightarrow 2 Na(g) + 1/2 O_2(g)$$
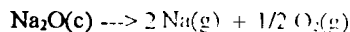
$$a_{(O2)}^{0.5} = a_{(Na2O)}/a_{(Na)}^2 \exp[-\Delta G^0/RT]$$

The free energy of the dissociation is $\Delta G_a^0(T) = (633,290 - T* 336.9856)$ J/(mole-K) from thermodynamic tables.(Wagman et al, 1982)

The sodium pressure at the solid electrolyte surface can be related to the current density of the AMTEC cell (Kennard, 1938)

$$P_{(Na)} = (2pM_{Na}RT)^{1/2} j/F$$

where M$_{Na}$ is the molecular weight of Na in kg/mole, R is the gas constant, j is the current density in A/m2, and F is the Faraday. The flux of oxygen from the surface can similarly be

related to the equilibrium vapor pressure of oxygen over the solid surface (Kennard, 1938)

$$J_{(O2)} = P_{(O2)}/(2pM_{O2}RT)^{1/2} , moles/sec$$

The activity of Na(g) and O2(g) over Na2O at 1298K can be calculated

$$\Delta G_a^0(1298K) = 389.253 \text{ Kj}$$

$$a_{(Na)}^{2*} a_{(O2)}^{0.5}/a_{(Na2O)} = \exp[-G_a^0/RT]$$

At 1298 K, in the absence of an external source of 02 or Na, a$_{(Na)}$= 2a$_{(O2)}$, a$_{(Na2O)}$=). Standard pressure is 10^5 Pa at unit activity, so P$_{(O2)}$ = 10^5 x a$_{(O2)}$ and the pressure of O₂ over Na₂O is 99 Pa at 1298K, and the O₂ flux is J$_{O2}$ < 1.347 X 10^{19} molecules/(m2-s).The pressure of O₂ over a phase such as beta alumina in equilibrium with Na₂O can be expressed similarly, using the relationship between activities given above, and the dependence of sodium activity on AMTEC device current density;

$$J_{(O2)} < 10^{25} F^{-4} a_{(Na2O)}^2 \exp[-2 \Delta G_a^0/RT]/((2pRT)^{2.5} M_{O2}^{0.5} M_{Na}^2 j^4).$$

From H. Nafe, a$_{(Na2O)}$=exp[DG$_b$/RT] =exp[(-149740J/mole + 39.4098J/(mole-K)*T)/RT].(Nafe, 1996) At 1298K and at only 10 A/m2, a condition where moderately fast beta decomposition occurs:

$$J_{(O2)} < 3.857x10^{-7} moles/(m^2-s) \text{ 0112.2 moles/(m}^2\text{-yr)}$$

The loss of O₂ is very strongly activated and also strongly dependent 011 the AMTEC cell's discharge current. However in the limit of small cell discharge currents, sodium pressure due to shunt currents and the sodium wiper pressure at the condenser will dominate, so that eliminating the discharge current will not lead to immediate rapid O₂ loss from the condenser. This is in part the reason fOr the inequality in the expression above. The Na₂O activity is determined by the free energy of formation of the beta phase from its constituent oxides, a$_{(Na2O)}^2$ = exp[-ΔG$_b$/RT], so

$$J_{(O2)} < 10^{25} F^{-1} \exp[(-\Delta G_b - 2 \Delta G_a^0)/RT]/(2pRT)^2 \cdot{}^5 M_O^{0.5} M_{Na}^2 j^4$$

and we can quantify the free energy change DG$_T$(T) for the disproportionation of beta alumina to alpha alumina, O$_{2(g)}$, and Na$_{(g)}$:

$$\Delta G_T(T) = \Delta G_b + 2 \Delta G_a^0 = (1416321 - .713381*T) kJ/mole$$

as 1673K, but does not seem to occur at a substantial rate in Na-BASE at lower temperatures (Hodge, 1983; You The phase diagram for the Na-Al-O system under reducing conditions has been evaluated and the equilibrium vapor pressure of O₂ calculated to be very low.(Yokokaw et al, 1995) The loss of oxygen from free Na₂O or from beta" alumina with no crystallographic phase change or a phase change to beta alumina would still be strongly activated, but may have a lower

activation energy. Interconversion of the beta and beta" alumina phases has been studied at temperatures as low ng blood et al, 1977) In related experiments, we found the amount of K-beta-alumina, initially at about 1-2%, to increase to about 3-4% after 500 hours at 1200K in about 2-7 Pa potassium vapor.(Williams et al, 1995) However, it could not be determined if this was due to conversion of the beta"-alumina phase or of amorphous material, and the conversion appeared to complete in the first 100 hours of the experiment, based on the conductivity change. Recent experimental data on the chemistry and thermodynamic properties of beta and beta" alumina deal with effect of conductivity, high sodium activity, and discriminate between the beta and beta" phases.(Nnfe, 1996; Rog et al 1992; Fritz et al, 1993) Kinetics of change in conductivity of Na-BASE and K-BASE in high temperature low pressure sodium vapor show a brief decrease in conductivity, followed by a longer period in which conductivity does not change.(Williams et al, 1995) There is no detectable composition change in the Na-BASE, but the amount of the beta phase increases very slightly in the K-BASE, although the majority phase remains K beta"-alumina. The reverse reaction, by which alpha alumina is attacked by sodium or potassium to form beta (and beta") alumina has been characterized at lower temperatures (T<700C) much more thoroughly than the disproportionation reaction of beta alumina, which is derived from thermochemical measurements. "The alumina/alkali metal reaction has been addressed to the point of a general consensus among researchers in the field.(Fink, 1978; Jung et al, 1983; van Reine, 1984; de With, 1985; Anderson, 1979; Susnitzky and Carter, 1985; Criado, 1981; van Hoek, 1992) While the disproportionation reaction should not proceed under conditions where the alkali metal attack on alpha alumina occurs, little information on either reaction at very low alkali metal pressure exists.

Metal Corrosion by Na$_2$O in Na$_{(l)}$.

of formation which exceeds the magnitude of the free energy of solution of the constituents in each other. Then the alloy formation is exothermic and the metal atoms are bound more strongly than in the pure constituents. This is true for many intermetallic compounds includi Metals which react/dissolve in liquid sodium or in liquid sodium containing dissolved sodium oxide can be divided into four groups, moving to the left across the periodic table.

(1) Electronegative lower melting metals typified by gold and silver which dissolve in pure sodium whether or not sodium oxide is present. Other lower melting metals such as aluminum and zinc dissolve in liquid sodium, but have miscibility gaps with liquid sodium at their melting points.(Hansen, 1958)

(2) Metals such as iron and nickel which form ternary oxides with sodium which have limited stability at both high and lower temperature: these ternaries can shuttle the metal to the cold zone where it crystallizes, releasing sodium oxide to the hot zone to dissolve more metal, and hence are corrosion problems. We have observed the dissolution and recrystallization of a nickel mesh in oxide-containing sodium in a demountable test cell experiment lasting about 100 hours at

about 1150K. In contrast, in experiments up to 1800 hours in length at up to 1100K, and briefer, hotter experiments, ordy surface alteration (which may have been deposition, and may have been substantially affected by cleaning procedures after the experiments) of stainless steel, inconel, molybdenum, and niobium were observed. Data suggests that niobium and tantalum may be in group (2), although they are much more resistant to corrosive dissolution than Fe and Ni.(Foust, 1972; DiStefano, 1989)

(3) Metals such as Mo which form very stable ternaries with sodium and oxygen like Na$_2$MoO$_4$, which can probably move to the cold zone without precipitating metal.

(4) Metals which reduce sodium oxide in sodium to form binary oxides and are hence oxygen getters such as Zr and Hf.

It is likely that corrosion is an issue for long term AMTEC life, but high temperature corrosion must be substantially more important than low temperature corrosion which is either very slow m insignificant due to kinetic limitations, given the very long periods of operation of lower temperature alkali metal loops with pure alkali metals. Filling in reliable, referenced informal ion which addresses all the corrosion issues in AMTEC cells is difficult, and the literature on corrosion of metals by alkali metals and alkali metals containing oxygen is substantial, although in many places contradictory, and not easily accessible or well reviewed Confusion has not decreased substantially with the passage of time for metal corrosion issues. One reference cited in Foust suggested high nickel solubility in sodium with little effect of oxygen concentration; a second experiment with apparently more careful control of dissolved oxide levels showed substantial oxygen dependence of nickel solubility but a much lower solubility at low oxygen levels (Foust, 1972) The solubility of iron in sodium has been shown repeatedly to depend substantially on oxygen concentration in the sodium (Foust, 1972) Some recent reports show high corrosion of molybdenum in sodium at relatively low temperature, while some other and I apparently more careful work indicates that molybdenum is among the most resistant of transition metals to sodium corrosion, even when some sodium oxide is present (DiStefano, 1989) DiStefano gives a good overview of the mechanisms involved in corrosive processes in alkali metals, with particular attention to Nb, Ta, Mo, and W.(DiStefano, 1989)

The dissolution of metals from alloys differs from dissolution from the pure metal in two respects. First, the alloy may very well have a substantial negative free energy ng most of the materials known as superalloys. Some of these, for example, contain aluminum, a metal which is fairly volatile in the pure state, but is much more tightly held in the superalloys. Another example observed at JPL in the intermetallic compound formed when Mn liberated by steel volatization at high temperatures reacts with W, dissolved, resulting in formation of separate phases, one of which sinters to large grain size and is largely composed of Mn, and the other is mostly W and maintains a small grain size. We saw this effect in relatively brief enough test cell experiments

where the hottest steel component was the heat shield support at about 600-700C and the electrodes were at 800-900C. It became obvious when we analyzed electrodes from exposure test cells in which the steel container was nearly as hot as the electrode. Clearly, Mn does not leave this alloy as fast as it leaves steel, or the problem would not exist.

Even when the react ion or dissolution thermodynamics rrre known, kinetic limitation may reduce rates to levels far below those expected from the thermodynamics alone. Uphill reactions at standard state may proceed quickly if a reaction product is removed, since then the product dots not attain its standard state activity. This is very important for AMTEC, where loss of volatile constituents mav drive reactions.

Accelerated Testing

Three methods will be investigated at JPL for accelerated life testing of AM TEC cell components. These are 1) increased temperature, 2) increased sodium flow rate, and 3) increased oxygen content in the liquid sodium. These are not expected to have similar effects on all processes; in particular increased temperature may give fairly limited acceleration and acceleration rates may only be determined after substantial testing, flow rate increases will amplify concentration gradients, bat may lead to erosion processes if increased too greatly, and increased corrosion due to oxygen concentration effects m a y completely alter the mechanisms of corrosion compared with a pure sodium system.

ACKNOWLEDGEMENTS

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